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Microgels and coating compositions containing same

Abstract:

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A microgel comprising a cross-linked copolymer of from 95.0 to 99.9 mole per cent of mono-ethylenically unsaturated monomer, at least 50% of which is a lower alkyl ester of methacrylic acid, and from 5.0 to 0.1 mole per cent of a cross-linking agent containing at least two ethylenic double bonds, the microgel having a swelling ratio in toluene of from 2 to 6 and being essentially free of substantially uncross-linked polymer having a viscosity average molecular weight greater than 200,000, may be prepared by heating at a temperature of from 40 DEG to 100 DEG C., an aqueous dispersion of the monomers until the swelling ratio in toluene of the resulting microgel is from 2 to 6 and, during the reaction, adding to the dispersion a water immiscible solvent or a chain-transfer agent to inhibit the formation of substantially uncross-linked polymer having a viscosity average molecular weight greater than 200,000. Lists of cross-linking agents and lower alkyl methacrylates and other mono-ethylenically unsaturated monomers are given. In the preferred process, the monoethylenically unsaturated monomer or monomers, the cross-linking agent and known initiators and emulsifiers are dispersed in water and the emulsion is then heated at a temperature of 40 to 110 DEG C. until the polymerization is 80 to 95% complete. Then at least 25%, and preferably 25 to 100% by weight based on the weight of monomers, of water-immiscible solvent for the monomers is added to the reaction mixture and the polymerization is continued until the polymerization is 95 to 100% complete. Alternatively the water-immiscible solvent may be added to the initial charge. Alternatively in the first mentioned preferred method a chain transfer agent may be added instead of the solvent, among those mentioned are thiophenols, carbon tetrabromide, ethylbenzene, pentaphenylethane and ethylthioglycollate. Data supplied from the esp@cenet database - Worldwide

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PATENT SPECIFICATION

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DRAWINGS ATTACHED.

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COMPLETE SPECIFICATION.

Microgels and Coating Compositions Containing Same.

We, E. I. DU PONT DE NEMOURS AND COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
This invention relates to microgels of lower alkyl esters of methacrylic acid and to coating compositions formulated therewith.
Lacquers based on the lower alkyl esters of methacrylic acid have found wide use in recent years because they can be applied to substrates and dried to form films and coatings which have outstanding durability and gloss retention. Such lacquers conventionally contain as the principle film-forming constituent substantially linear homopolymers or copolymers of lower alkyl esters of methacrylic acid in solution in an organic solvent. These conventional lacquers usually must be applied at solids concentrations ranging from 10 to 20%. If higher solids concentrations are used, the resulting lacquers are much too viscous to be applied by conventional procedures and form rough, uneven coatings.

Conventional organosols, that is, suspensions of particles of linear polymer in volatile organic liquid, offer several advantages over conventional solution-type lacquers in that they can be prepared at much higher solids concentrations as fluid compositions. However, known organosols of polymers of lower alkyl esters of methacrylic acid are subject to several disadvantages. First, they are generally unstable and the polymers therein settle, particularly if the organosols are warmed. Furthermore, at polymer concentrations of 20 to 40% the organosols also are fairly viscous, are poorly atomised by conventional spraying techniques and generally form rough and uneven films and coatings. When organosols are brush coated, masses of polymer collect in front of the brush leaving polymer-free volatile organic liquid behind. Also, coatings of organosols often must be extensively buffed to bring out their gloss.

Microgels and coating compositions formed therefrom have many of the advantages of organosols, yet do not have several of the aforementioned disadvantages. For example, they can be formulated into high-solids, fluid compositions which are stable. "Microgel" as used herein refers to particles of colloidal dimensions, for example, 0.05 to 1 micron in diameter as de-

terminated by light scattering or with an electron microscope, which are formed by gelation within polymer-monomer particles in emulsion or suspension polymerization. The microgels consist of high molecular weight (of the order of 10^8 to 10^{10}) molecules which contain points of crosslinkage and are comparable in size to the emulsion or suspension particles in which they are formed. Strong solvents cause these particles to swell but do not destroy the crosslinked structure thereof. Known dispersed systems of microgels in solvents, that is microsols, have not; however, been suitable for coating compositions. For example, when such microsols are spray coated, the resulting coatings are rough, uneven and have numerous blisters or "pop" marks.

We have found microgels which do not have the aforementioned disadvantages and which can be formulated into compositions which can be applied to yield smooth, tough, mar-resistant films and coatings and which are stable and have a high solids concentration.

The microgels of this invention comprise a crosslinked copolymer of from 95 to 99.9, and preferably from 99.5 to 99.9, mole per cent of mono-ethylenically unsaturated monomer, at least 50% of which is a lower alkyl ester of methacrylic acid, and from 5 to 0.1, and preferably from 0.5 to 0.1, mole per cent of crosslinking agent containing at least two ethylenic double bonds, the microgel having a swelling ratio in toluene of from 2 to 6, and preferably 3 to 4, and being essentially free of substantially uncrosslinked polymer having a viscosity average molecular weight of greater than 200,000. "Substantially uncrosslinked polymer" as used herein refers to polymers which are predominantly linear or branched as contrasted to the crosslinked network in the microgel particles. When a microgel of this invention is mixed with acetone or 2-ethoxyethyl acetate and centrifuged as described hereinafter, the substantially uncrosslinked polymer remains in solution while the microgel particles settle.

The coating compositions of this invention are microsols, that is, lyophilic dispersed systems containing solvent and, as the essential film-forming constituent, at least one of the aforementioned microgels. In these microsols the microgels form a molecularly heterogeneous dispersed system. The substantially unimolecular microgel particles because of their size give the microgels a cloudy or milky appearance. Rigorously speaking, the microsols are really solutions.

The monoethylenically unsaturated monomers used in preparing the microgels of this invention consist of at least 50 mole per cent, and preferably 70 to 100 mole per cent, of at least one lower alkyl ester of

methacrylic acid, that is, at least one ester formed from methacrylic acid and a 1 to 8 carbon atom alkanol. Such esters include, for example, methyl methacrylate, ethyl methacrylate, *n*-propyl methacrylate, isopropyl methacrylate, *n*-butyl methacrylate, *n*-amyl methacrylate, 2-ethylhexyl methacrylate, and *n*-octyl methacrylate. Other copolymerizable ethylenically unsaturated monomers can be mixed therewith in minor proportions. Such monomers are, for example, acrylic acid, methacrylic acid, the 1 to 4 carbon atom (that is, methyl to butyl) esters of acrylic acid, vinyl acetate, vinyl propionate, vinyl chloride, styrene, isobutylene, propylene, ethylene, acrylonitrile, methacrylonitrile, allyl chloride, itaconic acid and mixtures thereof. Microgels having a monoethylenically unsaturated component consisting of esters of 1 to 4 carbon atom alkanols with methacrylic acid and, particularly, methyl methacrylate are preferred.

Examples of crosslinking agents containing at least two ethylenic double bonds which can be used in this invention are ethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, methylene bisacrylamide, methylene bismethacrylamide, divinyl benzene, vinyl methacrylate, vinyl crotonate, vinyl acrylate, divinyl acetylene, trivinyl benzene, glycerine trimethacrylate, pentaerythritol tetramethacrylate, triallyl cyanurate, divinyl ethane, divinyl sulfide, divinyl sulfone, hexatriene, triethylene glycol dimethacrylate, diallyl cyanamide, glycol diacrylate, ethylene glycol divinyl ether, diallyl phthalate, divinyl dimethyl silane and glycerol trivinyl ether. Methacrylic acid esters of diols as well as methacrylamide derivatives of difunctional amines are preferred. Ethylene glycol dimethacrylate and methylene bismethacrylamide are particularly preferred because they react rapidly and crosslink efficiently when present in small amounts.

As stated hereinbefore, the microgels of this invention have a swelling ratio in toluene of from 2 to 6, and preferably 3 to 4. This property of the microgels is critical. Microgels which have a swelling ratio of less than 2 have very little affinity for solvents or polymer solutions and cannot be made into stable microsols in which the microgels do not flocculate or settle. Microgels having a swelling ratio in toluene of greater than 6, for example, 10 to 20, swell greatly in microsols formulated therewith making the resulting compositions viscous and difficult to apply. Furthermore, in such microsols at practical solids concentrations, the microgels absorb such a large portion of the solvent that there is not sufficient solvent left to disperse the microgel and any pigment or other additives mixed therewith. This latter problem becomes particularly

apparent and acute when wet coatings of such microsols are applied.

The swelling ratio of the microgels of this invention in toluene is determined from the equation:—

$$R = \frac{\text{specific viscosity}}{2.5 C.}$$

wherein R is the swelling ratio and C is the grams of microgel per gram of microsol. Specific viscosity is determined by a method analogous to that set forth in A.S.T.M. Specification D 1243-54. Briefly, 0.4 gram of microgel are dispersed in 50 milliliters of toluene and heated at 100° C. for about 30 to 60 minutes. Next, toluene is added to the dispersion to bring the total volume to exactly 100 milliliters. The kinematic viscosity of the dispersion and of toluene are then determined with a Ubbelohde Series U—1.0 viscometer in accordance with A.S.T.M. Specification D 445. The specific viscosity is the ratio of the kinematic viscosity of the microgel dispersion to the kinematic viscosity of toluene, minus one.

As stated hereinbefore, the microgels of this invention must be essentially free from substantially uncrosslinked polymer. Initially, during the polymerization of the monoethylenically unsaturated monomer and crosslinking agent, substantially linear polymers are formed. These polymers grow as the polymerization reaction continues linking monofunctional monomer with crosslinking agent primarily through one ethylenic double bond of the crosslinking agent. As the reaction proceeds toward completion and the number of pendent, unreacted double bonds (that is, the unreacted double bonds in the crosslinking agent) in the polymer molecules becomes relatively high with respect to the number of molecules of monomer, the crosslinking reaction which involves free radical attack on the pendent ethylenic double bonds in the growing or dead chains is favored. This latter reaction forms a branched and finally a crosslinked microgel particle. It has now been discovered that toward the end of the reaction as the crosslinked microgel is formed, minute but significant portions of high molecular weight substantially uncrosslinked linear polymer are formed. Unless special precautions are taken to limit this reaction which forms substantially uncrosslinked polymers, the resulting products are not useful for microgel coating compositions.

The accompanying drawing is a semi-logarithmic plot which correlates the maximum permissible weight fraction of substantially uncrosslinked polymer in the micro-

gels of this invention with the molecular weight of the substantially uncrosslinked polymer. Microgels having a concentration of uncrosslinked polymer having a viscosity average molecular weight above 200,000 and fallink within the shaded Area A in the graph can be formulated into coating compositions which have excellent application properties, and can be coated into substrates to form smooth, tough, mar-resistant films and coatings. Microgels having a concentration of substantially uncrosslinked polymer falling within the unshaded Area B, when formulated into coating compositions, yield coatings which are rough, blistered, uneven and extremely difficult to apply. It should be noted that the permissible concentration of substantially uncrosslinked polymer having a viscosity average molecular weight of above about 200,000 is extremely small in comparison to the total weight of microgel; for example, the maximum permissible weight fraction of substantially uncrosslinked polymer having a viscosity average molecular weight of 500,000 is about 5×10^{-3} , that of polymer having a viscosity average molecular weight of 1,800,000 is about 1×10^{-3} and that of polymer having a viscosity average molecular weight of about 4,500,000 is about 5×10^{-4} . It is thus evident that the terms "essentially free of substantially uncrosslinked polymer having a viscosity average molecular weight of greater than about 200,000" refers to microgels in which the uncrosslinked polymer falls within the shaded Area A in the drawing. Since the microgels having the requisite swelling ratio are usually at least about 80 to 90% converted to crosslinked polymers, points above a weight fraction of about 0.20 have little meaning.

The amount and molecular weight of substantially uncrosslinked polymer can be determined by first dispersing about 5 parts by weight of the microgel in about 95 parts by weight of acetone or 2-ethoxyethyl acetate, then centrifuging the resulting dispersion under a centrifugal force of about 60,000 times the force of gravity until substantially all of the microgel particles settle or at least until some clear supernatant centrifugate is formed. The solids concentration of the centrifugate, which is a solution of the substantially uncrosslinked polymer, is determined by evaporating an aliquot portion thereof. This determination yields the concentration of substantially uncrosslinked polymer. The viscosity of a similar aliquot portion of the centrifugate is measured and the molecular weight determined therefrom by the Staudinger equation:

$$M = K \left(\frac{\eta_{sp}}{C} \right)^{1/a} = 7.9 \times 10^5 \left(\frac{\eta_{sp}}{C} \right)^{1.43}$$

wherein M is the viscosity average molecular weight, C is the concentration of polymer in grams per 100 millimeters of solution and $\frac{\eta_{sp}}{C}$ is the specific viscosity of the

centrifugate.

The products of this invention are prepared by forming an aqueous emulsion of monoethylenic unsaturated monomer and crosslinked agent, heating the emulsion at a temperature of about from 40 to 100° C., until the reaction is substantially complete to yield a microgel having a swelling ratio of from 2 to 6 and, during the reaction, adding to the reaction mixture an agent to inhibit the formation of high molecular weight substantially uncrosslinked material.

Considering a preferred process of this invention in more detail, first monoethylenically unsaturated monomer, crosslinked agent together with suitable well known initiators and emulsifiers are dispersed in water. Although charges containing up to 70% of copolymerizable material can be used, preferably the charge consists of from 25 to 50% by weight of copolymerizable materials. Any of the conventional anionic, cationic or nonionic emulsifiers and water soluble initiators can be employed. Examples of emulsifying agents are sodium lauryl sulfate, lauryl pyridine chloride, polyoxyethylene, polyoxypropylene, colloidal silica, anionic organic phosphates, magnesium montmorillonite, the reaction product of 12 to 13 moles of ethylene oxide with 1 mole of octyl phenol, secondary sodium alkyl sulfates and mixtures thereof. Usually from 0.25 to 4% of emulsifier based on the total weight of reactants is used. Examples of initiators are potassium persulfate, sodium persulfate, ammonium persulfate, tertiary butyl hydroperoxide, hydrogen peroxide, azo bis(isobutyronitrile), azo bis(isobutyroimidine hydrochloride), various redox (reduction-oxidation) systems such as hydrogen peroxide and ferrous sulfate and well known persulfate-bisulfate combinations. Usually, from 0.05 to 5% by weight of initiator based on the weight of copolymerizable monomers is used.

Next, the emulsion containing the copolymerizable monomers, initiator and emulsifier is heated at a temperature from 40 to 110° C. until the polymerization is from 80 to 95, and preferably from 85 to 90% complete. The completeness of the reaction can be determined by placing a 0.5 gram sample of the reaction mixture in a 2-inch evaporating dish, heating the sample in a circulating hot air oven for 1 hour at 110° C. and then weighing the resulting sample to determine the solids concentration in the reaction mixture. At this point, at least 25%, and preferably from 25 to 100% by weight of water-immiscible solvent for the monomers such

as, for example, toluene, benzene, ethylene dichloride, chloroform or a mixture thereof, based on the weight of monomers, is added to the reaction mixture. The polymerization is continued at the same temperature, and preferably at the reflux temperature, until the polymerization is 95 to 100% complete.

A variant of the aforementioned procedure is to add at least 25%, and preferably 25 to 100% by weight of the aforementioned water-immiscible solvent based on the weight of monomers to the initial charge. In this case, the reaction can be run substantially to completion without further addition of modifying agents.

Alternately, the first of the aforementioned procedures can be carried out but instead of adding solvent near the end of the polymerization, a chain-transfer agent can be added. At least 0.05%, and preferably from 0.05 to 1% of chain-transfer agent based on the weight of monomers is usually used. Preferably the chain-transfer agent is also added in two portions, one portion when the polymerization is 85 to 90% complete and the second portion when the polymerization is 90 to 95% complete. These chain-transfer agents inhibit the formation of long chain substantially uncrosslinked polymers by terminating chain growth and transferring the active centers of polymerization to other polymer chains. Active chain transfer agents such as, for example, thiophenol, substituted thiophenols such as 4-methylphenyl mercaptan, C_2 to C_6 alkyl mercaptans such as tertiary amyl mercaptan, *n*-butyl mercaptan, ethyl mercaptan and isopropyl mercaptan, carbon tetrabromide, ethyl benzene, pentaphenyl ethane, ethyl thioglycolate and mixtures thereof which have a chain-transfer constant of greater than about 0.1 are preferably used. Chain-transfer constants are defined by Paul J. Flory in "Principles of Polymer Chemistry", Cornwall University Press, Ithaca, New York, Page 138 et seq. (1953).

A still further variant for the aforementioned general procedure is to prepare an aqueous emulsion at a temperature of from 40 to 100° C. of a small portion of monoethylenically unsaturated monomer, at least 50% of which is a lower alkyl ester of methacrylic acid, from 5 to 0.1 molar proportion of a crosslinking agent containing at least two ethylenic double bonds and from 0.25 to 1 mole of chain-transfer agent per mole of crosslinking agent, then add the remaining monoethylenically unsaturated monomer (the total amount of the latter being from 95 to 99.9 molar proportions) at a rate substantially equal to that at which it is polymerized. A convenient method for determining the rate at which the monoethylenically unsaturated monomer is to be added is

to run the reaction at the reflux temperature, usually at about 90° C., and add the monomer at a rate sufficient to maintain the exothermic reaction at reflux. Another convenient method for determining the rate of addition is to add the monomer at a rate sufficient to maintain the exothermic reaction at a temperature between 40 and 100° C.

After the reaction has run to completion, the resulting microgel is separated and dried. A convenient procedure is to filter the microgel, then tray, drum or spray dry the resulting product. Alternatively, the wet product can be dispersed in a non-solvent such as hexane, and azeotropically distilled to remove entrained water. The dried microgel usually has a particle size of from 0.05 to 1 micron, and preferably from 0.1 to 0.3 micron. If suspension polymerization, rather than emulsion polymerization, is used whereby somewhat larger particles are obtained the microgel is preferably ground to bring the particle size within the aforementioned range.

Microgels of this invention prepared as described above can be formulated into coating compositions by merely mixing them with the common lacquer solvents and diluents conventionally used for preparing lacquers of lower alkyl esters of methacrylic acids such as, for example, esters such as ethyl acetate, butyl acetate or 2-ethoxyethyl acetate; ketones such as acetone, methyl ethyl ketone, or methyl isobutyl ketone; alcohols such as ethanol, 2-propanol or *n*-butanol; ethers such as ethylene glycol monobutyl ether; hydrocarbons such as toluene, xylene or naphtha or mixtures thereof. However, preferably the microgels are mixed with a solution of another organic film-forming material denoted hereinafter as a matrix polymer. Examples of matrix polymers which can be used as part of the microgel compositions, that is, microsols, of this invention, are nitrocellulose; cellulose acetate butyrate; cellulose acetate; copolymers of vinyl chloride containing a major portion (usually at least 85% by weight) of vinyl chloride and a minor portion of, for example, vinyl acetate, vinylidene chloride, acrylonitrile, or maleic, fumaric or acrylic acid or their esters; linear homopolymers and copolymers of the aforementioned lower alkyl esters of methacrylic acid; amino-aldehyde resins such as those formed by the reaction of polyamines such as, for example, melamine and urea with aldehydes such as formaldehyde, acetaldehyde and furfural, particularly the etherified derivatives thereof such as butylated urea formaldehyde and melamine formaldehyde resins and similar alkylated materials; oil modified alkyd resins; and polyepoxy polyhydroxy resins. The critical requirement of the matrix polymer is that it be soluble and

compatible with the microgel, that is, the microgel must be able to form a lyophilic dispersed system in the matrix polymer and in dried coatings. Although as little as 20% of microgel based on the total weight of the film-forming constituent can be used in the aforementioned compositions, in order to gain full advantage of the high solids concentration imparted to coating compositions formulated therewith, it is usually preferred to use from 50 to 75% of microgel and 25 to 50% of matrix polymer.

As is conventional in the art, other well known modifiers such as pigments and extenders, plasticizers and flow-control agents can be added to the compositions of this invention in conventional amounts. Examples of pigments and extenders are metal oxides, hydroxides, chromates, silicates, sulfides, sulfates, carbonates, carbon blacks, organic dyes and the lakes thereof and metal flake pigments. Examples of plasticizers are ditetrabutylthiodisuccinate, butyl phthalyl mixed benzoic acid and fatty-oil acid esters of pentaerythritol, poly(propylene adipate) dibenzoate, diethylene glycol dibenzoate, tetrabutylthiodisuccinate, butyl phthalyl butyl glycolate, acetyl tributyl citrate, dibenzyl sebacate, tricresyl phosphate, toluene ethyl sulfonamide, di(2-ethyl hexyl)ester hexamethylene dipthalate, di(methoxycyclohexyl) phthalate, dibutyl phthalate triphenyl phosphate, 2-ethylhexyl benzyl phthalate dicyclohexyl phthalate and benzyl phthalate. As is obvious from the aforementioned discussion, additives which destroy the lyophilic nature of the microsols should be excluded.

The microgels of this invention are characterized by their ability to be formulated into coating compositions having a high solids concentration and which can be applied by any of the conventional coating techniques such as roller, brush and particularly spray coating techniques to yield uniform, smooth, tough, mar- and print-resistant coatings. Typically, for example, microgel coating compositions of this invention contain at least 50% more organic film-forming material per unit weight of composition than conventional lacquers based on lower alkyl esters of methacrylic acid. Coating compositions containing the microgels of this invention can be used in any of a wide variety of applications in which conventional lacquers based on lower alkyl esters of methacrylic acid are now used yielding films and coatings with substantially equivalent excellent durability and gloss retention.

The following examples are intended to illustrate this invention and not to limit it in any way. Parts and percentages are by weight unless otherwise specified.

EXAMPLE I.

The following materials are charged to a 130

reaction vessel, agitated to form a uniform dispersion and heated in a nitrogen atmosphere at 60° C. for about 115 minutes:—

		Parts
5	Distilled water	4,800
	Methyl methacrylate	2,400
	Ethylene glycol dimethacrylate ...	48
	Secondary sodium alkyl sulfate dispersing agent ("Tergitol" (Trade Mark) 7—Union Carbide & Carbon Corporation)	18
10	Potassium persulfate (4% aqueous solution)	60

At this point the reaction is approximately 90% complete. Next, 24 parts of tertiaryamyl mercaptan chain-transfer agent and 0.6 part of azobisisobutyronitrile catalyst dissolved in 10 parts of methyl methacrylate are added to the reaction mixture and the reaction is continued at 60° C. for an additional 25 minutes. At this point, the reaction is about 95% complete. Finally, the resulting microgel is blown with air to remove residual tertiaryamyl mercaptan, filtered through a felt spectrum and tray dried at room temperature. An 88% yield of microgel having a particle size of about 0.174 microns determined by light scattering techniques, a swelling ratio of 3.2 and about 4% of substantially uncrosslinked polymer having a molecular weight of 120,000 is obtained. The swelling ratio and amount and molecular weight of substantially uncrosslinked polymer are determined as described hereinbefore.

Preparation and Evaluation of Coating Compositions.

A clear coating composition is prepared by dispersing 525 parts of the microgel described above in a solution of 200 parts of a homopolymer of methyl methacrylate having a relative viscosity of 1.15, (determined in accordance with A.S.T.M. Specification D 445-46T, Method B, at 25° C. in a Modified Ostwald Viscosimeter, Series 50) in 1375 parts of a solvent mixture consisting of 20% of toluene, 10% of methyl isobutyl ketone, 20% of hexane, 30% of xylene, 5% of butanol and 15% of 2-ethoxyethyl acetate.

A pigmented coating composition is also prepared by dispersing 525 parts of the microgel and 294 parts of benzyl butyl phthalate in a solvent mixture similar to that used in the clear coating composition and mixing therewith a solution of 75 parts of a copolymer of 98 parts of methyl methacrylate and 2 parts of methacrylic acid and 135 parts of a homopolymer methyl methacrylate having relative viscosities of 1.130 and 1.143, respectively, determined as des-

cribed above. Next, the pigmented coating composition is completed by adding thereto a mill base consisting of 410 parts of titanium dioxide pigment dispersed in the same solvent. The solids concentration of the pigmented coating composition is about 33% by weight. Both the pigmented and clear compositions are free from settling after standing several months at room temperatures.

Steel panels treated with conventional rust inhibitor are prime coated with a conventional oil modified alkyd resin primer and sealed with a composition containing, as the principal film-forming constituent, the reaction product of phosphoric acid and a copolymer of methyl methacrylate and glycidyl methacrylate. The clear and pigmented coating compositions of this invention described above are sprayed over the primed and sealed steel panels and baked at about 93° C. for 30 minutes. The compositions have spray application properties substantially equivalent to those of conventional methacrylate lacquers applied at a concentration of 20% solids. Both of the coating compositions form smooth uniform coatings which are free from blisters or "pop" marks. Both coatings have excellent mar and print resistance and are tough and durable.

EXAMPLE 2.

An aqueous dispersion is prepared from the following materials:—

		Parts
	Distilled water	4,800
	Methyl methacrylate	2,400
	Ethylene glycol dimethacrylate ...	12
	Secondary sodium alkyl sulfate ...	18
	Potassium persulfate (4% aqueous solution)	60

The dispersion is heated at 60° C. until the reaction is approximately 85% complete. Next, 4 parts of thiophenol dissolved in 6 parts of toluene are added to the reaction mixture and heating is continued for 10 minutes at 60° C. At this point, the reaction is about 90% complete. Four more parts of thiophenol dissolved in 6 parts of toluene are added to the reaction mixture and heating is continued at 60° C. for an additional ten minutes until the reaction is about 95% complete. The resulting product is filtered and tray dried at room temperature to give a 94% yield of microgel having a particle size of about 0.195 microns, a swelling ratio of about 3.6 and containing 4.0% of substantially uncrosslinked polymer having a viscosity average molecular weight of 100,000.

A clear coating composition is prepared

by dispersing 35 parts of the microgel prepared above in 65 parts of the solvent mixture described in the preceding example, mixing therewith 10 parts of a homopolymer of methyl methacrylate dissolved in 50 parts of the same solvent and spraying the resulting composition onto panels similar to those described in the preceding example. The coating composition has properties similar to those of the clear coating composition described in Example 1.

An aqueous dispersion is prepared by the same procedure used in this example from 4,800 parts of water, 2,400 parts of methyl methacrylate, 12 parts of ethylene glycol dimethacrylate, 18 parts of secondary sodium alkyl sulfate dispersing agent and 60 parts of potassium persulfate initiator (4% aqueous solution). The reaction mixture is heated at about 60° C. until the reaction is about 98% complete, then the resulting microgel is filtered and dried as previously described. The resulting microgel has a swelling ratio of about 7.4 and contains 3% of substantially uncrosslinked polymer having a viscosity average molecular weight of about 1,000,000. When this microgel is formulated into coating compositions and sprayed, the coating compositions are deposited in large droplets ranging from $\frac{1}{4}$ to $\frac{1}{2}$ inch in diameter. Dried films of the microgel are uneven and are covered with "pop" marks or blisters. This comparative microgel is indicated by the point X in the drawing.

EXAMPLE 3.

An aqueous dispersion is prepared from the following materials:—

	Parts
40 Distilled water	1,200
Methyl methacrylate	600
Ethylene glycol dimethacrylate ...	3
Secondary sodium alkyl sulfate dispersing agent	18
45 Potassium persulfate initiator (4% aqueous solution)	60

The reaction mixture is heated at 60° C. for 169 minutes until the reaction is about 85% complete. Next, 300 parts of toluene are added to the reaction mixture which is then heated to the reflux temperature, about 85° C., while 230 parts of toluene-water binary is distilled therefrom over a period of about one hour. The resulting microgel is filtered and tray dried at room temperature. The product has a swelling ratio of 3.2, about 4% of substantially uncrosslinked polymer having a viscosity average molecular weight of about 100,000 and particle size of about 0.143 microns.

The microgel just described is formulated into a coating composition from the following materials:—

	Parts	65
Microgel	15	
Cellulose acetate butyrate ($\frac{1}{2}$ second viscosity)	5	
Titanium dioxide pigment	10	
Tricresyl phosphate plasticizer	5	70
Solvent	65	

The resulting coating composition can be sprayed or brushed readily onto substrates to yield smooth, uniform coatings which have outstanding durability and gloss retention and are free from blisters or "pop" marks.

EXAMPLE 4.

An aqueous dispersion is prepared from 6,300 parts of water, 16.2 parts of sodium lauryl sulfate, 4.2 parts of tertiarybutyl hydroperoxide and heated to 90° C. Next, 300 parts of a mixture of 2,025 parts of methyl methacrylate, 136.8 parts of ethylene glycol dimethacrylate and 754.8 parts of benzyl butyl phthalate, together with 63 parts of lauryl mercaptan are added thereto. The resulting reaction mixture is held at the reflux temperature for about 3 hours by adding small portions of the aforementioned methyl methacrylate/ethylene glycol dimethacrylate/benzyl butyl phthalate/lauryl mercaptan mixture to the reaction mixture. During this period, the temperature of the reaction mixture rises from about 88 to 98° C. Finally, the unreacted monomer is azeotropically distilled from the reaction mixture, then the microgel is filtered and dried. The resulting microgel has a swelling ratio of about 2.9 and contains only a trace of substantially uncrosslinked polymer having a molecular weight of about 100,000.

EXAMPLE 5.

An aqueous dispersion is formed from the following materials:—

	Parts	105
Distilled water	400	
Methyl methacrylate	200	
Ethylene glycol dimethacrylate ...	1.4	
Secondary sodium alkyl sulfate dispersing agent	1.5	110
Potassium persulfate initiator (4% aqueous solution)	5	
Benzene	100	

The reaction mixture is agitated under a nitrogen atmosphere for 4 hours at 60° C.

until the reaction is about 97.2% complete. The resulting microgel is then filtered and dried. The resulting product has a swelling ratio of about 2.5 to 3.0 and contains less than about 4% of substantially uncross-linked polymer having a viscosity average molecular weight of 100,000.

If 4 parts of methacrylic acid or 10 parts of styrene are substituted for an equal weight of the methyl methacrylate used above, and this example is repeated, microgels with properties substantially similar to those described are obtained.

EXAMPLE 6.

The procedure of Example 3 is repeated except that 6 parts of methylene bismethacrylate is substituted for the ethylene glycol dimethacrylate used in that example. The resulting microgel has a particle size of about 0.167 microns, a swelling ratio of about 4 and has a quantity of substantially uncrosslinked copolymer falling within Area A of the graph in the drawing.

EXAMPLE 7.

An aqueous dispersion is formed from the following materials:—

	Parts
Distilled water	1,200
Methyl methacrylate	420
Ethyl acrylate	180
Ethylene glycol dimethacrylate	9
Secondary sodium alkyl sulfate	4.5
Potassium persulfate initiator (4% aqueous solution)	15

The aqueous dispersion is heated at 60° C. for 130 minutes, then 300 parts of toluene are added thereto and refluxed at 85 to 92° C. for 45 minutes while 235 parts of toluene-water binary are removed. The resulting microgel is then filtered and dried to yield a product having a swelling ratio of about from 4 to 6 and less than about 5% of substantially uncrosslinked polymer having viscosity average molecular weight of less than about 150,000.

EXAMPLE 8.

The following materials are charged to a reaction vessel, agitated to form a uniform dispersion and heated in a nitrogen atmosphere at about 60° C. for about 75 minutes:—

	Parts
Distilled water	1,200
Butyl methacrylate	600
Ethylene glycol dimethacrylate	9
Secondary sodium alkyl sulfate dispersing agent	9
Potassium persulfate (4% aqueous solution)	15

At this point about 1 part of thiophenol dissolved in about 5 parts of toluene is added to the reaction mixture and heating is continued at 60° C. for an additional 10 minutes. Finally, about 1 more part of thiophenol dissolved in about 5 more parts of toluene is added and heating is again continued at about 60° C. for 20 more minutes. The resulting reaction mixture is filtered and dried to yield a microgel having a swelling ratio of 5.4 and containing about 10% of substantially uncrosslinked polymer having an average molecular weight of less than about 160,000.

A coating composition is prepared by blending a microsol of 50 parts of the microgel described above, 65 parts of acetone and 65 parts of toluene with a mill base of 5 parts of carbon black pigment dispersed in 5 parts of nitrocellulose and 10 parts of benzyl butyl phthalate. The resulting coating composition can be sprayed or brushed onto substrates and dried to yield smooth, uniform coatings which are free from blisters or "pop" marks.

EXAMPLE 9.

An aqueous dispersion is prepared from the following materials:—

	Parts
Distilled water	1,200
Methyl methacrylate	480
Methyl acrylate	120
Ethylene glycol dimethacrylate	9
Secondary sodium alkyl sulfate dispersing agent	4.5
Potassium persulfate initiator (4% aqueous solution)	15

The reaction mixture is heated at 60° C. for 205 minutes, then 300 parts of toluene are added thereto and the reaction is continued at reflux until 252 parts of distillate are removed therefrom over a period of about 45 minutes. During the distillation, the reaction temperature rises from about 83 to 95° C. The resulting product has a particle size of 0.15 microns, a swelling ratio of about from 4 to 6 and contains an amount of substantially uncrosslinked polymer falling within Area A of the graph shown in the drawing.

If 10 parts of triethylene glycol dimethacrylate are substituted for the ethylene glycol dimethacrylate used in this example, substantially similar results are obtained.

EXAMPLE 10.

This example illustrates coating compositions of this invention containing a variety of matrix polymers.

The microgel described in Example 1 is

blended with the indicated materials to yield coating compositions having the following formulations:—

<i>Composition A.</i>			
			<i>Parts</i>
5	Microgel	...	50
	Cellulose acetate butyrate ($\frac{1}{2}$ -second viscosity)	...	50
	Methyl isobutyl ketone	...	150
10	Isopropanol	...	50
	Toluene	...	50

<i>Composition B.</i>			
			<i>Parts</i>
	Microgel	...	50
15	Copolymer of 90% of vinyl chloride and 10% of vinyl acetate	...	50
	Methyl isobutyl ketone	...	150
	Isopropanol	...	50
	Toluene	...	50

<i>Composition C.</i>			
			<i>Parts</i>
	Microgel	...	50
	Homopolymer of methyl methacrylate (relative viscosity, 1.15)	...	50
25	Benzyl butyl phthalate	...	40
	Acetone	...	150
	Toluene	...	50

<i>Composition D.</i>			
			<i>Parts</i>
30	Microgel	...	50
	Copolymer of 98% of methyl methacrylate and 2% of methacrylic acid (relative viscosity, 1.15)	...	50
	Benzyl butyl phthalate	...	40
35	Acetone	...	150
	Toluene	...	50

<i>Composition E.</i>			
			<i>Parts</i>
	Microgel	...	50
40	Homopolymer of methyl methacrylate (relative viscosity, 1.15)	...	50
	Nitrocellulose ($\frac{1}{2}$ -second viscosity)	...	20
	Dibutyl phthalate	...	30
	Carbon black pigment	...	5
45	Acetone	...	100
	Toluene	...	100

In preparing Composition E, preferably a mill base is formed with the nitrocellulose, the carbon black pigment, the dibutyl

phthalate plasticizer, and, if desired, a small portion of the solvent; a solution of the polymer of methyl methacrylate is mixed with the mill base; then the resulting composition is mixed with a microsol of the microgel and solvent.

Each of the coating compositions described above can be sprayed or brushed onto substrates and dried to yield smooth, uniform coatings which are free from blisters or "pop" marks. Also, instead of the microgel of Example 1 used above, any of the other microgels described in the other preceding examples can be used in similar coating compositions with similar results.

WHAT WE CLAIM IS:—

1. A microgel which comprises a cross-linked copolymer of from 95.0 to 99.9 mole per cent of mono-ethylenically unsaturated monomer, at least 50% of which is a lower alkyl ester of methacrylic acid, and from 5 to 0.1 mole per cent of a crosslinking agent containing at least two ethylenic double bonds, the microgel having a swelling ratio in toluene of from 2 to 6 and being essentially free of substantially uncrosslinked polymer having a viscosity average molecular weight of greater than 200,000.

2. A microgel according to Claim 1, in which the copolymer is formed from 99.5 to 99.9 mole per cent of the mono-ethylenically unsaturated monomer and 0.5 to 0.1 mole per cent of the crosslinking agent.

3. A microgel according to Claim 1 or 2, in which at least 50% of the mono-ethylenically unsaturated monomer is methyl methacrylate.

4. A microgel according to any of Claims 1 to 3, having a swelling ratio of from 3 to 4.

5. A microgel according to any of Claims 1 to 4, in which the crosslinking agent is ethylene glycol dimethacrylate or methylene bismethacrylamide.

6. A coating composition which comprises a lyophilic dispersion in liquid organic vehicle of at least one microgel according to any of Claims 1 to 5.

7. A coating composition which comprises a lyophilic dispersion in a polymeric solution of at least one microgel according to any of Claims 1 to 5.

8. A coating composition according to Claim 7, in which the polymeric solution contains from 25 to 50 parts by weight of a linear polymer of methyl methacrylate and 50 to 75 parts by weight of microgel, the monoethylenically unsaturated monomer from which the microgel was formed being methyl methacrylate.

9. A process for the production of a microgel which comprises forming an aqueous dispersion of from 95 to 99.9 molar proportions of mono-ethylenically unsatur-

ated monomer, at least 50% of which is a lower alkyl ester of methacrylic acid, and from 5 to 0.1 molar proportions of a cross-linking agent containing at least two ethylenic double bonds, heating the resulting dispersion at a temperature of from 40 to 100° C. until the swelling ratio in toluene of the resulting microgel is from 2 to 6 and, during the reaction, adding to the dispersion a water immiscible solvent or a chain-transfer agent in order to inhibit the formation of substantially uncrosslinked polymer having a viscosity average molecular weight of greater than 200,000.

10. A process according to Claim 9, in which from 25 to 100%, based on the weight of the monomers, of a water immiscible solvent for the monomers is added to the dispersion when the reaction is from 80 to 95% complete and the reaction is continued until the swelling ratio in toluene of the resulting microgel is from 2 to 6.

11. A process according to Claim 9, in which from 0.05 to 1% of chain-transfer agent based on the weight of the monomers is added to the dispersion when the reaction is from 80 to 95% complete and the reaction is continued until the swelling ratio in toluene of the resulting microgel is from 2 to 6.

12. A process for the production of a microgel which comprises forming an aqueous dispersion of from 95 to 99.9 molar proportions of ethylenically unsaturated monomer, at least 50% of which is a lower alkyl ester of methacrylic acid, from 5 to 0.1 molar proportions of a crosslinking agent containing at least two ethylenic double bonds, and from 25 to 100% by weight based on the weight of the monomers of a water immiscible solvent therefor and heating the resulting reaction mixture until the swelling ratio in toluene of the resulting microgel is from 2 to 6.

13. A process for the production of a microgel which comprises adding to water at a temperature of from 40 to 100° C. with agitation, a small proportion of the mono-ethylenically unsaturated monomer, at least 50% of which is a lower alkyl ester of methacrylic acid, from 5 to 0.1 molar proportions of a crosslinking agent containing at least two ethylenic double bonds, and from 0.25 to 1 mole of chain-transfer agent per mole of cross-linking agent, and then adding the remaining mono-ethylenically unsaturated monomer (the total amount of the latter being from 95 to 99.9 molar proportions) at a rate substantially equal to that at which the monomer is polymerised and continuing the reaction until the swelling ratio in toluene of the resulting microgel is from 2 to 6.

14. A process according to any of Claims 9, 11 or 13, in which the chain-transfer agent is thiophenol, 4-methylphenyl mercaptan, an alkyl mercaptan containing from 2 to 6 carbon atoms, carbon tetrabromide, ethyl benzene, pentaphenyl ethane or ethyl thioglycolate.

15. A microgel according to Claim 1 substantially as herein described in any of Examples 1 to 9.

16. A process for the production of a microgel according to any of Claims 9 to 14 substantially as herein described in any of Examples 1 to 9.

17. A coating composition according to Claim 6 substantially as herein described in any of Examples 1—3, 8 or 10.

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967051

COMPLETE SPECIFICATION

1 SHEET

*This drawing is a reproduction of
the Original on a reduced scale*

